PROJETO DE GRADUAÇÃO

VALIDATION OF A SAMPLING UNIT FOR VAPORS EXTRACTION FROM THE *STYX* *INTEGRATED PYROLYSIS REACTOR*

Por,
Lívia Timponi Brandini

Brasília, 16 de Dezembro de 2013.

UNIVERSIDADE DE BRASILIA

FACULDADE DE TECNOLOGIA
DEPARTAMENTO DE ENGENHARIA MECANICA

UNIVERSIDADE DE BRASILIA
Faculdade de Tecnologia

Departamento de Engenharia Mecânica

PROJETO DE GRADUAÇÃO

VALIDATION OF A SAMPLING UNIT FOR VAPORS EXTRACTION FROM THE *STYX INTEGRATED PYROLYSIS REACTOR*

POR,

Lívia Timponi Brandini

Relatório submetido como requisito parcial para obtenção
do grau de Engenheira Mecânica.

Banca Examinadora

Prof. Carlos Alberto Gurgel Veras, UnB/ENM
Orientador _____

Profa. Thaís Maia Araújo, UnB/FGA
Examinadora _____

Profa. Grace Ferreira Ghesti, UnB/IQ
Examinadora _____

Brasília, 16 de Dezembro de 2013.

Dedicatória

Aos meus pais, Cristina e Adhemar.

Lívia Timponi Brandini

Agradecimentos

Em primeiro lugar, gostaria de agradecer imensamente aos meus pais, Cristina e Adhemar, a quem dedico este trabalho, por todo o carinho, paciência, inspiração, orientação e apoio incondicional ao longo de toda a minha vida. Tenho certeza que não teria chegado até aqui se não fosse pelo incentivo, valores e educação que sempre recebi de ambos.

Agradeço principalmente ao meu orientador, Carlos Alberto Gurgel, pela disposição em me orientar nesta área de pesquisa relativamente nova e ainda incipiente no Departamento de Mecânica, me dando a chance de desenvolver um projeto de meu interesse. Agradeço também pelas reuniões decisivas em momentos de dificuldade ao longo do projeto.

Sou muito grata também ao CNPq, por ter me contemplado com uma bolsa de intercâmbio acadêmico do Programa Ciência sem Fronteiras para a Alemanha durante um ano, no Edital de 2012/2013. Foi essa experiência que me possibilitou desenvolver o presente trabalho no Instituto Tecnológico de Karlsruhe (KIT).

Gostaria de agradecer ainda ao Mr. Leibold – chefe do Instituto de Engenharia Química da KIT – pela oportunidade de estagiar no Centro de Pesquisa de Karlsruhe. Sou profundamente grata ao meu supervisor, Mr. Tomasi, de quem recebi apoio e orientação incondicionais ao longo dos meses de estágio. Além disso, foi um enorme prazer poder trabalhar com o Mr. Richter, Mr. Schieber e Mr. Lelièvre.

Agradeço também ao Italo, meu companheiro de desafios, por me tranquilizar e me animar em momentos de tensão e angústia, me fazendo acreditar na minha capacidade de realização.

Aos meus eternos amigos de universidade, Milzara, Felippes e Renatha que me acompanharam de perto nesta difícil jornada que é a Engenharia Mecânica e estiveram presentes em momentos importantes do curso.

A toda a minha turma do 1º/2008 e amigos veteranos, pelo clima de descontração, diversão e leveza, mesmo nas horas de puro desespero coletivo!

Aos meus amigos do peito e familiares queridos, agradeço pelo apoio às minhas decisões profissionais, e pela compreensão quando eu não pude estar presente nos últimos meses por estar extremamente envolvida com o Projeto de Graduação.

Lívia Timponi Brandini

ABSTRACT

This report describes the goals, achievements, results and conclusions of my four months experimental internship at the Institute of Technical Chemistry (ITC), from the Institute of Technology of Karlsruhe (KIT), in Germany. The theme of this work is the validation of a sampling system for vapors extraction in the STYX Pyrolysis Plant, designed and built at the ITC. Parallel to this experimental work at the plant, laboratory experiments for product analysis were also conducted by means of a TGA and a GC-MS equipment in order to substantiate decisions related to this main task, as well as to assist in other aspects of the wide research project about the STYX.

RESUMO

Este relatório descreve os objetivos, realizações, resultados e conclusões do meu estágio experimental de quatro meses no Instituto de Engenharia Química (ITC), do Instituto Tecnológico de Karlsruhe (KIT), na Alemanha. O tema deste trabalho consiste na validação de um sistema de amostragem para a extração de vapores da Planta de Pirólise STYX, projetada e construída no próprio ITC. Paralelamente ao trabalho experimental na planta, experimentos laboratoriais para análise de produtos foram conduzidos por meio de equipamentos de Análise Termogravimétrica (TGA) e de Cromatografia de Gases e Espectrometria de Massas (GC-MS) com o propósito de embasar decisões relativas a essa principal tarefa, assim como para auxiliar em outros aspectos do amplo projeto de pesquisa da Planta STYX.

SUMMARY OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

k	Chemical reaction rate constant	
E	Activation energy	
A	Pre-exponential factor	
R	Boltzmann gas constant	$[J \cdot K^{-1} \cdot mol^{-1}]$
Cp	Calor especifico a pressão constante	[kJ/kg.K]
m	Mass	[kg]
n	Reaction order	
T	Temperature	[^{o}C]
$\dot{Q}$	Heating Rate	[K/min]
P	Proportional parameter	
I	Integrative parameter	
D	Derivative parameter	
T	Time	[min or s]

Greek Symbols

α	Normalized form of mass loss data of decomposed sample

Chemical Elements and Compounds

C	Carbon
CH_4	Methane
CO	Carbon Monoxide
CO_2	Carbon Dioxide
H	Hydrogen
H_2	Hydrogen Gas
H_2O	Water or steam
N	Nitrogen
O	Oxygen
O_2	Oxygen Gas

Subscripts

0	Initial
f	Final
i	Instantaneous

Superscripts

$\bullet$	Temporal variation

Acronyms

ESP	Electrostatic Precipitator
GC	Gas Chromatography
ITC	Institut für Technische Chemie (Institute of Technical Chemistry)
KIT	Karlsruher Institut für Technologie (Institute of Technology of Karlsruhe)

MS	Mass Spectrometry
TGA	Thermogravimetric Analysis
THF	Tetrahydrofurane

1 INTRODUCTION

This chapter gives a brief introduction about the STYX Integrated Pyrolysis Plant and introduces the goals of this work.

This internship work – whose main theme is the validation of a sampling system for the extraction of vapors produced in the STYX Integrated Pyrolysis Plant – was carried out from 29.05.13 until 16.09.13 in the Institute of Technical Chemistry (ITC), located in the Research Center of KIT (Karlsruhe Institute for Technology, Campus Nord).

The STYX Integrated Pyrolysis Plant is a bench-scale screw type reactor developed at KIT that enables the production of tailored fuels from heterogeneous biogenic types of feedstock. Lately, the plant has been continuously optimized for processing biomass feedstock – although, for this study, only chopped beech wood has been used to feed the reactor.

A sampling unit was designed for extracting vapors samples from the STYX reactor. However, both its functionality and the sampling method needed to be tested, modified (if necessary) and validated.

1.1 OBJECTIVES

In this sense, the main goal of this internship was to ensure the proper and scientifically accurate extraction of clean or raw pyrolysis vapors at three different positions along the reactor, so that the chemical compounds formed by pyrolysis reactions among the process could be locally obtained and then analyzed by the GC-MS – a measuring equipment which performs "Gas Chromatography Mass Spectrometry". By means of these gas samples, it would be possible to compare the development in chemical kinetics model, based on lumped relevant species, with experimental data in order to validate the model for the bench-scale reactor.

However, during these three months, not only technical experimental work at the pyrolysis plant was executed, but also laboratory tests in the Thermogravimetric Analyser (TGA) and in the Gas-Chromatography/Mass Spectrometry (GC-MS) equipment were conducted. These secondary laboratory tasks were important to ground decisions for modifying some aspects of the original sampling method concept, as well as to provide a broader understanding of the goals and challenges related to the pyrolysis of biomass in the STYX research project.

2 LITERATURE REVIEW

This chapter features the main aspects related to Pyrolysis, the STYX Plant operation and the designed sampling system for vapors extraction. It also brings a short explanation about the TGA and the GC-MS analysis, as support experiments.

2.1 THE STYX INTEGRATED PYROLYSIS PLANT

The STYX Integrated Pyrolysis Plant (Figure 2.1) consists of a bench-scale screw pyrolysis reactor which is able to process organic matter feedstock (i.e. biomass) with hot gas integrated filtration.

Figure 2.1. STYX reactor opened for maintenance.

2.1.1 Pyrolysis Definition

Pyrolysis is the thermal degradation of organics in absence of oxygen.

This is an endothermic irreversible process that converts organic material into three main products classes: an energetic non-condensable gaseous phase (pyrolysis gas or permanent gas, mainly containing CO, CO_2 and CH_4); liquid phase products (condensable volatiles – water-like condensates and oil-like condensates, such as tars); and a solid residue rich in carbon (char).

Pyrolysis of biomass is the first stage to generate conditioned intermediates for heat and power generation , fuel production or gasification.

The relative percentage of these three products types depends on the adopted pyrolysis method and, hence, is also correlated to the conditions and operational parameters, that were conveniently chosen to drive the pyrolysis, according to the required goals for the process.

Pyrolysis can be divided into three major groups, characterized by the set heating rate:

- **Slow Pyrolysis (or Conventional)** - This type of process is also known as carbonization and aims to maximize the production of charcoal instead of liquid and gaseous products. It requires low temperature (around 400ºC) and long solids residence time.
- **Intermediate Pyrolysis** – The temperature in this process in moderate, about 500ºC and the hot vapors residence time is also moderate (from 10 to 20 seconds). Usually 50% of the products are liquid, 20% correspond to solid residue (char) and 30% refer to pyrolysis gas.
- **Fast Pyrolysis (or Flash)** - There are several fast pyrolysis technologies, but the main feature in all of this type is the focus on obtaining liquids and gases, preferably. The temperature is around 700ºC and the residence time of vapors is short (approximately 1 second).

The STYX plant is classified as intermediate pyrolysis, combining features of slow pyrolysis, i.e. residence time of solids in the range of minutes, and fast pyrolysis, i.e. short vapors residence time.

2.1.2 The STYX Pyrolysis Process

The plant includes a feeding system, an integrated auger where the screw conveyor is placed, filter candles, condensers, Electrostatic Precipitator (ESP) and gas detectors. A graphic representation of the STYX plant can be observed in Figure 2.2.

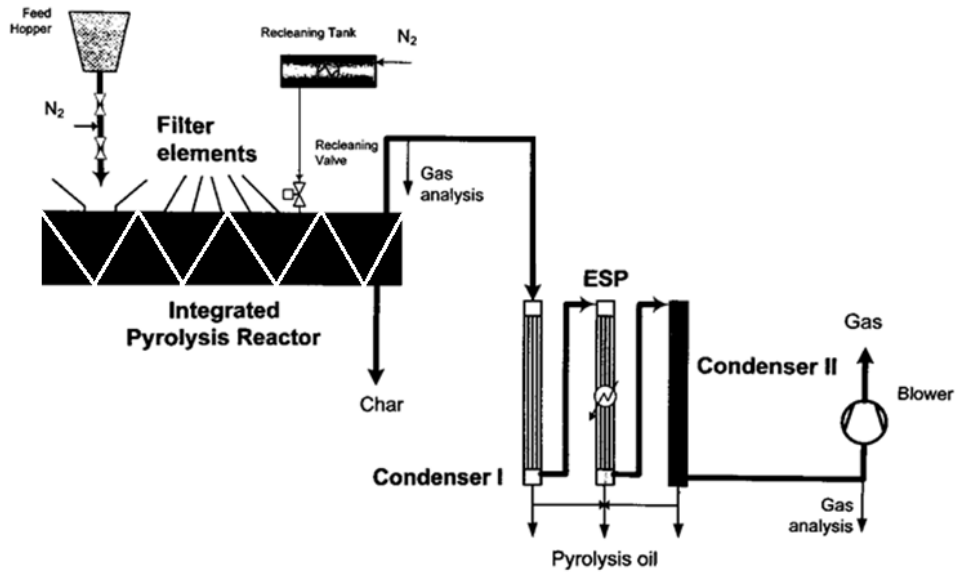

Figure 2.2 Illustrated scheme of the STYX Integrated Pyrolysis Plant.

First of all, the selected feedstock (in this case, beech wood) is introduced in the hopper. The mass flow rate of feedstock that comes into the system is controlled by the dosing screw. Then, by the rotation of the screw, the biomass is transported into the hot zone of the reactor, where the whole pyrolysis process takes place.

The residence time of feedstock can be adjusted by modifying the rotation speed of the screw. Nitrogen is supplied inside the plant as scavenging gas – most part is introduced from the feeding system – in order to avoid oxidation/combustion inside the reactor.

The residual char is discharged at the outlet under the reactor while the pyrolysis vapors go through a filter system to remove particulate matter at high temperatures, still inside the reactor. After the filter unit, the vapors are condensed and collected as pyrolysis condensate, while passing the condensers and the ESP. A small amount of permanent gas is conducted to a detector to be analyzed.

A blower placed at the end of the system is responsible for the extraction vapors from the reactor by maintaining a small pressure drop along the plant.

It is relevant to mention that the plant was designed for maximal mass flow rate of 5 kg/h and temperature range of 300-500ºC.

Some technical information of the plant are:

- Throughput: 10 kg/h
- Maximal Temperature: 500-600ºC
- Residence Time Range: 5-25 min
- Inside Pressure: ca. -2...-20 mbar
- Electric Heating Power: 40 kW
- Heated Length: 2000 mm
- Screw diameter: 150 mm

The operation parameters that were set in the plant for running the experiments were:

- Feedstock: Beech Wood
- Feeding rate: 2 kg/h
- Residence time: 10 min
- Temperature inside the reactor: 450ºC
- Nitrogen flow:
  - Char Tank - 3 L/min;
  - Reactor - 0 L/min;

- Filter compartment - 0 L/min;
- Feeding System - 11 L/min;
- Electrostatic Precipitator (ESP) - 4 L/min.

2.2 SAMPLING UNIT FOR VAPORS EXTRACTION

The sampling system (Figure 2.3) is composed by:

- Condenser – heat exchanger used to condensate hot pyrolysis vapors to pyrolysis condensate;
- Electrostatic precipitator (ESP) – particulate control device that applies electrical forces to move particulate matter (in solid, liquid or aerosol forms) entrained with the vapors onto collection surfaces;
- Regulation valve – used for adjusting the desired pressure drop in the sampling unit;
- Pressure Gage – indicates the low pressure right after the regulation valve;
- Filter – purifies the pyrolysis gas by removing the remaining particulate;
- Three-way-valve – depending on the valve opening, the gas is directed either to the flowmeter or to the gas detector;
- Flowmeter – analogic instrument for measuring the gas flow rate sucked by the pump as function as the applied pressure drop;
- Multi gas detector – electronic equipment that evaluates and informs the percentage of the main permanent gas compounds (CO, CO2, CH4);
- Three thermocouples – the first and the second thermocouples indicate the vapors temperature right before and after the condenser inlet and outlet, respectively; the third one is located after the pump and indicates the gas temperature before the 3-way-valve.

Figure 2.3. Sampling system for vapors extraction.

The configuration of the sampling system can be better understood by means of the flowchart represented in Figure 2.4.

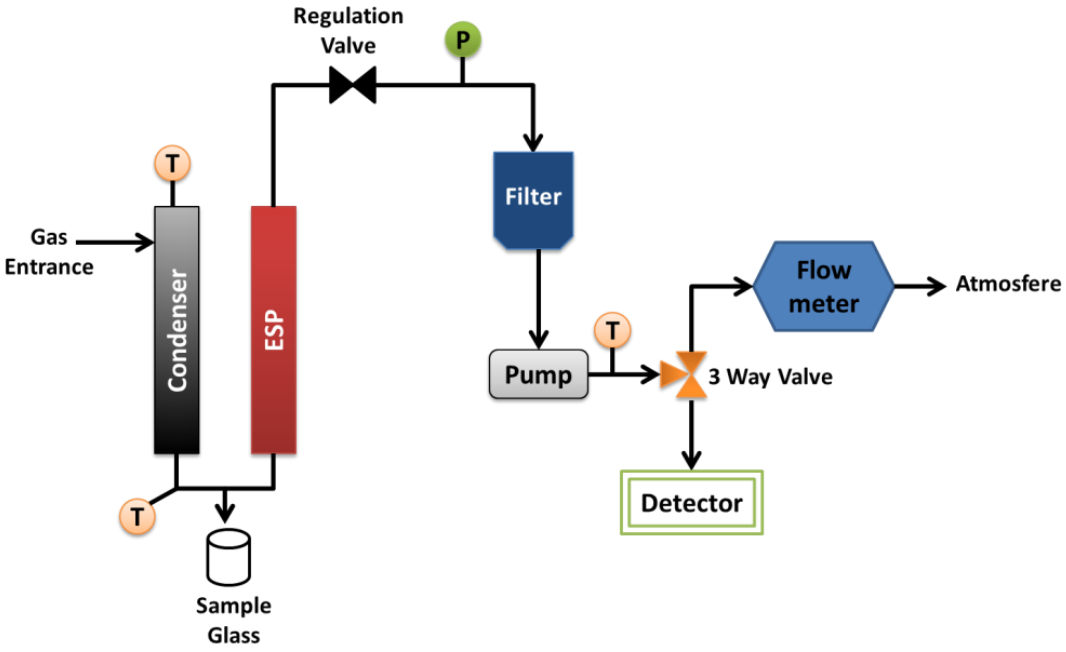

Figure 2.4. Sampling system flowchart.

By attaching the sampling system at the three different positions along the reactor (Figure 2.5), it is possible to take vapors samples from different stages of the process, and later, analyze them at the laboratory.

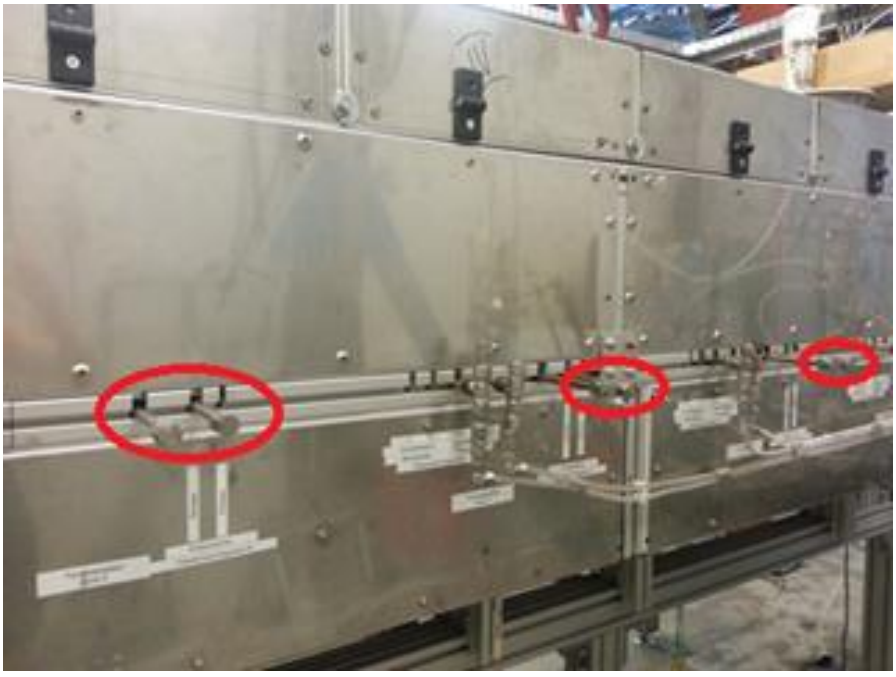

Figure 2.5. Three positions for vapors outlet.

2.3 THERMOGRAVIMETRIC ANALYSIS (TGA)

The Thermogravimetric Analysis (Figure 2.6) is one of the most widespread thermoanalytical measurement methods. By means of this method, the mass variation of a sample at controlled environmental conditions (heating rate, gas atmosphere…) is measured as a function of temperature.

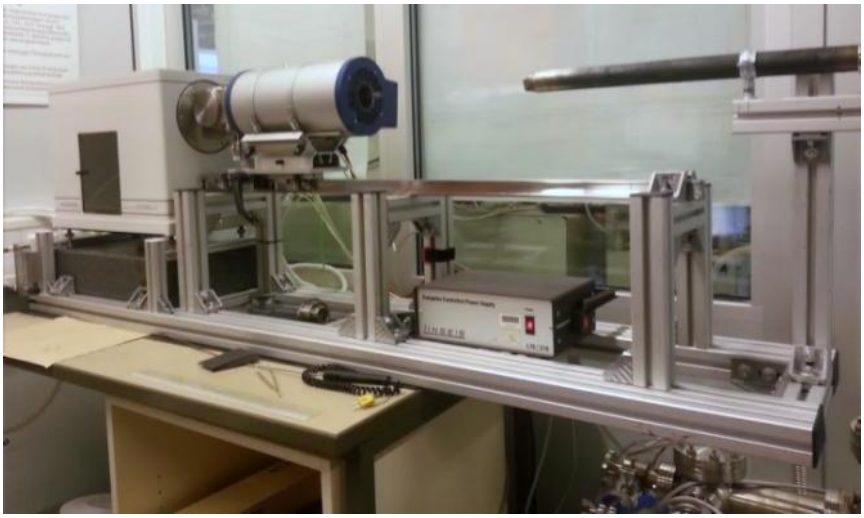

Figure 2.6. TGA equipment

The term "thermal analysis" refers to processes, in which samples are subjected/exposed to an imposed temperature change and, in the course of this heating, the temperature-induced properties modifications are recorded. The heating process is driven by an oven with controlled temperature program, which determines the temperature modifications in terms of time.

The thermogravimetric analysis also requires a microbalance (or thermal balance), which enables measuring the smallest changes in the 1µg range. The sample is initially charged in a small sample cup (crucible), which is later placed on a holder connected to the thermal balance. The sample support is placed inside a quartz tube together with a thermocouple for measuring the sample temperatures (Figure 2.7).

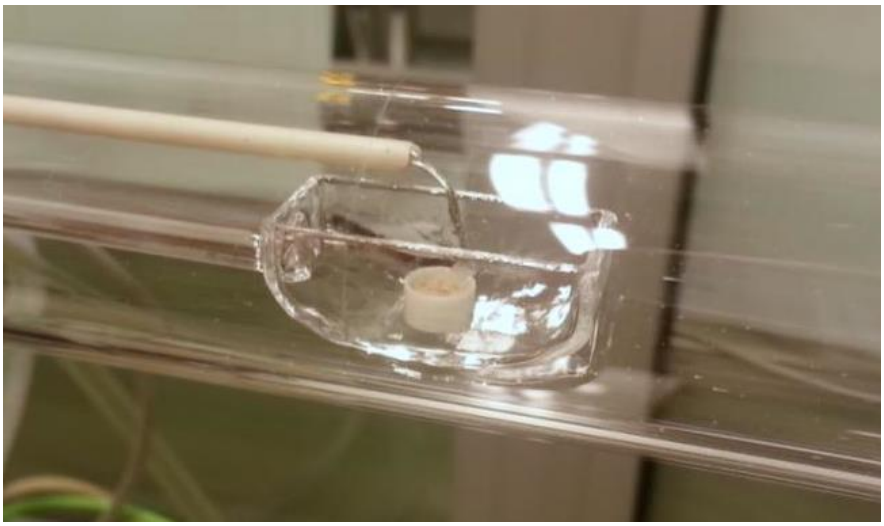

Figure 2.7. Sample crucible on holder inside the glass tube and below the thermocouple.

Before the test starts to run, it is extremely important to calibrate the thermal balance to obtain accurate values for initial and final sample masses, as well as the mass loss curve. Alternatively, an external precision balance can be also used for taking the initial and final masses; however, even in this case, the thermal balance should also be calibrated around zero and, thus, only the relative mass loss would be given and plotted by the software.

During a test, the sample is heated by means of an oven, which covers the sample holder, up to a desired change of temperature.

Both the thermal balance and the support for the samples are enclosed by a glass container, whereby it is later possible to inject a desired gas flow through the system. Since in this case the pyrolysis process of biomass is simulated in microscale, providing nitrogen gas flow is important to avoid matter oxidation. Thus, a nitrogen glass bottle and a flowmeter are also attached to the system.

The glass tube that surrounds the sample holder is movable – for properly placing and removing the sample crucibles –, and its safe fixation is provided by a metal screw plug attached to the glass tube end.

The Computer Controlled Power Supply Linseis L70/210 provide present-time information about the electrical power and heating rate signals, demanded for executing a desired test. This direct connection with the computer is indispensable for the data evaluation, since the current and temperature values should be read by the software, which governs the changes on power and heating rates according to the previously set heating program.

2.4 GC-MS ANALYSIS

The GC-MS Analysis combines Gas-liquid Chromatography (GC) and Mass Spectrometry (MS) to identify different substances within a test sample. The gas chromatography portion separates the chemical mixture into pulses of pure chemicals and, then, the mass spectrometer identifies and quantifies the chemicals. The GC-MS equipment is shown in Figure 2.8.

Figure 2.8. GC-MS equipment.

The GC separates chemicals based on their volatility, or ease with which they evaporate during the heating of the injected sample. In general, small molecules travel more quickly than larger molecules.

The MS is used to identify chemicals based on their structure. The spectrometer is capable of recognizing smaller and fragmented compounds resulting from the blasting with electrons and, consequently, ionization of the particles.

At the end, this information is sent to a computer and a mass spectrum (Figure 2.9) is created. The mass spectrum is a graph or diagram that contains various representative surfaces corresponding to the amount of these different masses that traveled through the filter.

```
File       : C:\HPCHEM\1\DATA\TOMASI_M\BW001_D1.D
Operator   : Tomasi
Acquired   : 11 Jul 2013   1:53 pm using AcqMethod PYROC300
Instrument :   GC/MS Ins
Sample Name: 2013.07.10-11- Dot
Misc Info  : 450°C 10min Stage 1 Rein
Vial Number: 1
```

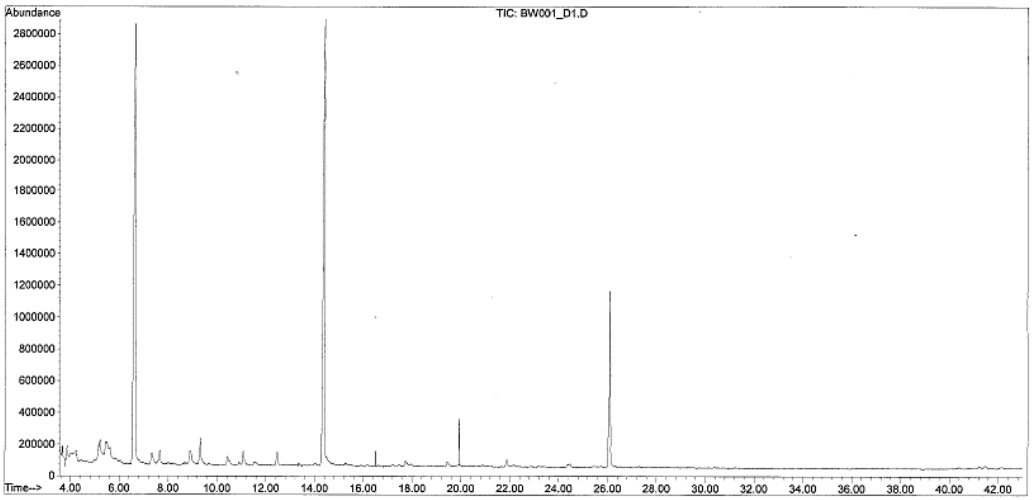

Figure 2.9. Mass Spectrum based on the analysis of one sample from the plant

However, the GC-MS software it is only able to quantify some reference species that have been previously cataloged – such as Furfural, Guaiacol and Phenol. The other species can only be recognized and compared to other known structures, but their areas cannot be properly correlated, thus, and amount of these substances cannot be estimated.

So, the GC-MS results were used for verifying the presence of some known species in the samples, which means “qualitative analysis”, and sometimes, for calculating the amount of this three reference species within a “quantitative analysis”.

3 METHODOLOGY

This chapter describes the methodology designed to achieve the proposed objectives, as well as the approach used to perform each experiment in question.

The initial intention of this research was to establish a global sampling method that could be identically applied to all the three different positions along the reactor. However, each stage has particular conditions, such volumetric flow rate suction (related to the pressure drop) and volatile amount to be condensed. So, the sampling parameters could not be exactly the same for different positions.

3.1 VALIDATION OF THE SAMPLING UNIT

In order to validate the sampling unit, a sampling method had to be specified and tested to guarantee that:

- the samples are always taken only locally without influencing the vapor-phase composition; that means, the chemical compounds present on the samples were formed by pyrolysis reactions at that reactor position, from where it was extracted;
- the experimental sampling method is repeatable.

With this purpose, the influence of the unit operation conditions during the sampling of vapors needed to be investigated. Since there was a known relationship between the pressure drop (ΔP) in the filter candles, the gas flow rate (sucked by the sampling unit) and the vapors condensate composition in the samples, a non-disturbing value for the applied flow rate had to be determined to avoid sucking vapors formed in other positions of the reactor, influencing the mixing of the vapor phase within the reactor.

Thus, some experiments at the plant were run for testing the maximal flow rate that should be used in the sampling system. Diverse flow rates, such as 2,5 L/min, 1,9 L/min, 1,8 L/min and 1,6 L/min were applied and their corresponding condensate samples were analyzed by the GC-MS. The samples color observation and the qualitative analysis of the spectra given by the GC-MS showed that 1,8 L/min should be the upper limit for locally sucking from the reactor, with the original arrangement of filter candles.

3.1.1 Description of the Initial Sampling Method

The sampling method defined and applied during the first sampling tests was based on the following steps. The idea was to ensure the proper assembly of the sampling system at the STYX reactor, as well as its repeatability.

1. Place the condenser in front of the desired reactor position to take the sample. For this, place the crane (Figure 3.1.a) – upon which the condenser is hung – next to the output and adjust the height by pressing the “up” or “down” button at the remote control (Figure 3.1.b).

Figure 3.1.a. Crane for supporting the condenser

Figure 3.2.b. Crane remote control

2. When the reactor is already running at steady state conditions and the gas outlet was already heated until 150°C by the attached heating purse, unscrew the plug of the gas output (Figure 3.2.a), insert the lance in the hole for unblocking the duct and, then, attach the condenser inlet by screwing its nut on the reactor outlet.

Figure 3.2.a. Clean and raw gas outlets

Figure 3.2.b. Condenser and ESP assembled

3. Turn on the electrical source (Figure 3.3) by pressing the power button and then activate the “High Voltage” at the red button. Increase the voltage until approximately 20 V and, if necessary, increase also the amperage in case of restricted voltage values. This source powers the ESP, which is connected after the condenser.

Figure 3.3. Electrical source for powering the ESP

4. Switch on the pump, which is required for the suction of the vapors into the sampling device. After that, when the suction and the ESP function are stable, switch the glass bottle for the new sampling bottle.

Figure 3.4.a. Pump powering device

Figure 3.4.b. Pump connected with electrical motors

5. Adjust the retention valve (Figure 3.5.a) for setting the desired pressure drop inside the ducts and, consequently, regulating the gas flow that runs through the volumetric flowmeter (Figure 3.5.b). Specifying the pressure drop is important to ensure that the extracted vapors were really produced locally.

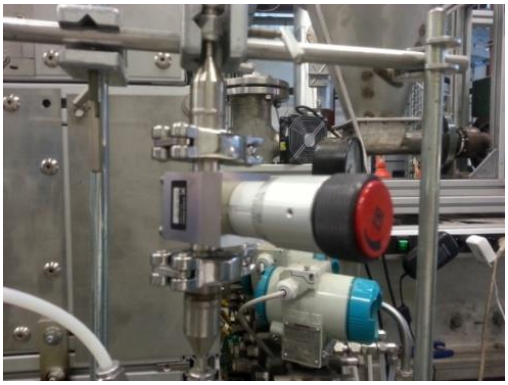

Figure 3.5.a. Valve for controlling the pressure drop

Figure 3.5.b. Volumetric counter for the gas inlet

6. Write down the temperature values shown by the thermometer connected to the thermocouples (installed before and after the condenser - Figure 3.6.a, Figure 3.6.b and Figure 3.6.c), as well as the pressure drop value and the source settings (current and voltage), shown in the Figure 3.6.d. The temperature conditions during the sampling should be well known because they influence directly the condensation rate coupled with decomposition kinetics).

Figure 3.6.a. Thermocouple before the condenser

Figure 3.6.b. Thermocouple after the condenser

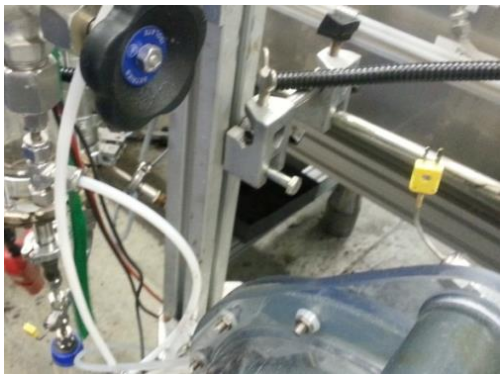

Figure 3.6.c. Thermocouple before volumetric counter

Figure 3.6.d. Thermocouple after the condenser

7. Write down the flow rate reported by the volumetric flowmeter (Figure 3.7). Switch the three-way-valve direction and plug the ducts to send the vapors to the gas detector, for measuring the percentage of CO, CO_2, CH_4 and O_2 in the gas sample. Write these values as well.

Figure 3.7. Flowmeter

8. Measure all the values mentioned before (temperatures, flow rate and gases percentage in the detector) three times during the sampling procedure, that should take approximately one hour in order to achieve the necessary amount of condensate.
9. Wait until the sampling bottle (Figure 3.8) is filled with an intermediate amount (aproximately 30g) of condensate and then switch off the pump and the electrical source, respectively.

Figure 3.8. Sampling bottle

10. Unplug the sampling inlet from the gas outlet, close it properly and, finally, take the sample bottle for the GC-MS analyzer (Figure 2.8).
11. The sampling device has to be properly cleaned with acetone after each test.

3.1.2 Subsequent Designed Methodology

After installing the sampling system and defining a repeatable sampling method for the vapors extraction, the final goal of this work was to make an experimental sampling campaign along the reactor (position 1, 2 and 3). The obtained samples would be tested in the GC-MS and the analysis results would be post-processed to conclude local mass balances and elemental balances (C/H/O).

However, the guidelines of this work have been sometimes rethought and, at certain point, modified due to some technical obstacles that were evident during the last months. These limitations and technical problems, as well as the providences taken to solve them are explained in the chapter of Results.

3.2 TGA TESTS

During the internship, the Thermo-gravimetric Analysis was carried out as part of the STYX Integrated Pyrolysis Plant research project, concerned to Pyrolysis of Biomass in the STYX Pyrolysis Plant.

The pyrolysis of biomass – more specifically, beech wood – has been investigated in this plant and the TGA can provide useful information to assist in the development of a pyrolysis model to be applied to the STYX Plant.

Based on curves generated by the TGA, important kinetic parameters can be calculated and used for testing models that simulate the real pyrolysis reactions that occur inside the plant.

The kinetic parameters are constants that appear in the kinetic rate expressions and are required to describe the rate of a reaction. For instance, for the simple global nth-order reaction with temperature dependence is described by the Arrhenius equation (1):

$$\frac{d\alpha}{dt} = k = Ae^{-\frac{E}{RT}}(1-\alpha)^n, \quad \text{with} \quad \alpha = \frac{m_0 - m_i}{m_0 - m_f} \tag{1}$$

where: k = chemical reaction rate constant; E = activation energy; A = pre-exponential factor; R = Boltzmann gas constant = 8,314472 $J \cdot K^{-1} \cdot mol^{-1}$; n = reaction order; T = temperature; α is the normalized form of mass loss data of decomposed sample; m_0, m_f and m_i refer to initial sample weight, final sample weight and sample weight at instant i.

The TGA tests provide values for the variables k, α and T. Since R is also a known constant, only the other three constants A, E and n should still be determined for describing the decomposition reaction of beech wood. This means that, with three different experimental data sets for the Arrhenius equation, it is possible to determine these unknown variables.

3.2.1 Test Preparation

Before beginning a TGA test, the following methodology is required:

I. Switch on, the computer, the TGA Power Source, the thermal balance controller, the gas flow pump, respectively. After that, adjust the nitrogen flow level to 10 L/min and initialize the software interface.

II. Set a time-temperature program to be executed during the test, by defining the heating rate up to each constant desired temperature, time interval for constant temperatures, etc. In this case, the constant temperatures intervals were usually at 250°C (drying temperature of biomass), 450°C, 500°C and 550°C (investigation of maximal work temperature for the STYX reactor).

III. Find out the best parameters combination (among proportional, derivative and integral values) to reach a stable sample heating and, consequently, a consistent heating curve. The input of these three parameters is required by the software to guide the calculation operation conditions. This is an iterative process between the user and the TGA software that requires time for seeking the optimal parameters set (Figures 3.9 and 3.10).

IV.

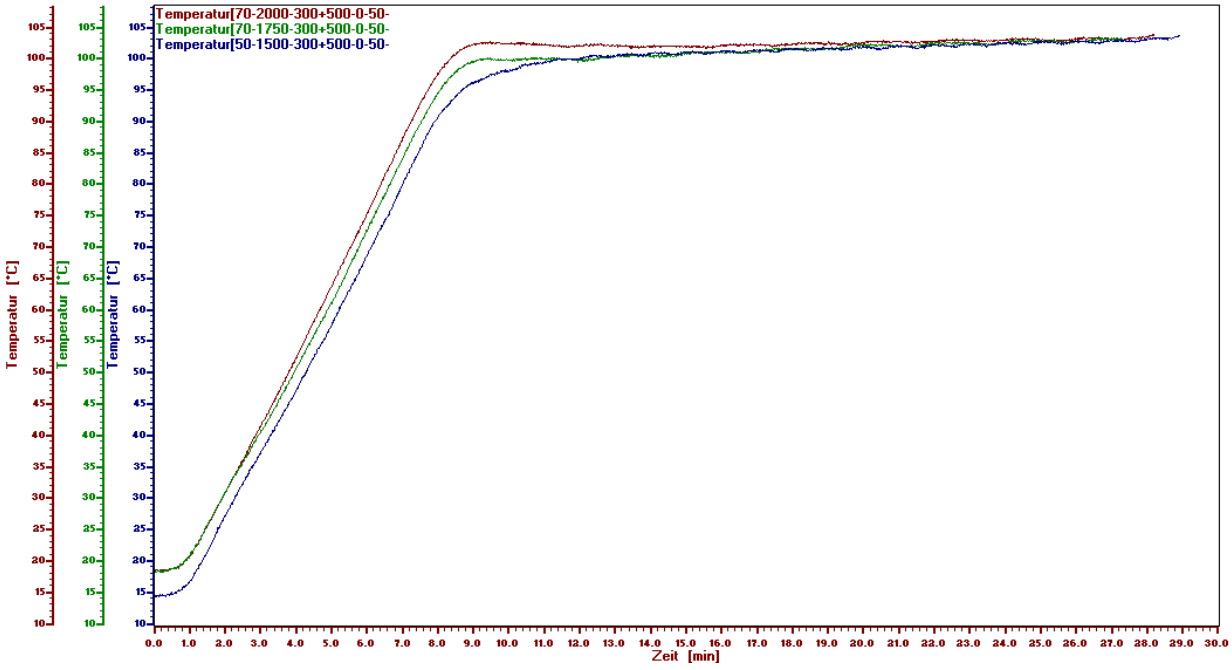

Figure 3.9. Parameters Combination trial for obtaining the desired heating curve up to drying temperature.

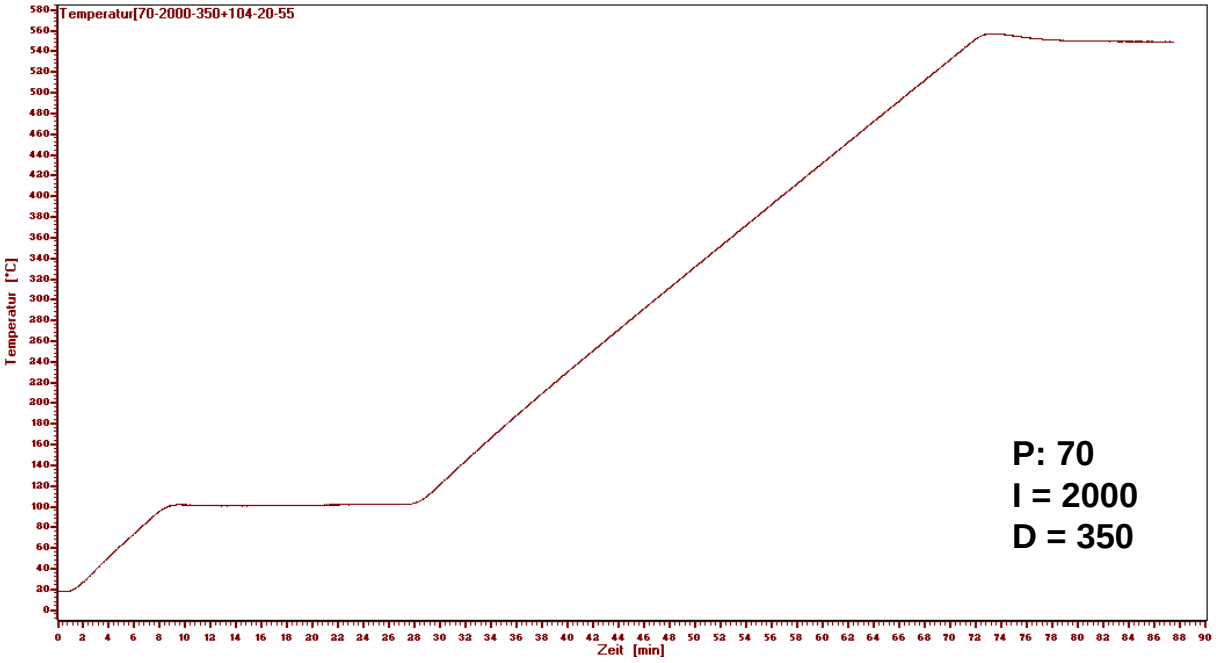

Figure 3.10. Optimal parameters combination for simulating the thermal processes inside the STYX up to 550ºC.

V. Weight the sample crucible empty and, then, weight again the crucible filled with milled biomass. Write down the net initial sample weight.

VI. Uncouple the glass tube from the TGA structure and carefully remove it.

VII. Place the sample crucible on the holder, centralized right under the thermocouple.

VIII. Attach the glass tube again and move the oven towards the tube. When the glass tube is completely covered by the oven, fix its position by lowering the security lock.

IX. Finally start the test by pressing "Ein" (Start Button) in the software interface. When the heating program is concluded, take back the oven towards the cooler and wait until its temperature return to the reference temperature. (Only after that, it is possible to begin a new test, if necessary.)

X. With a thermal glove, remove the glass tube again and take the sample out. Weight the crucible on an external precision balance again and write down the final sample weight.

XI. All the data was recorded by the computer, which enables the plotting of temperature curve and mass loss of the sample as function of time (Figure 3.11).

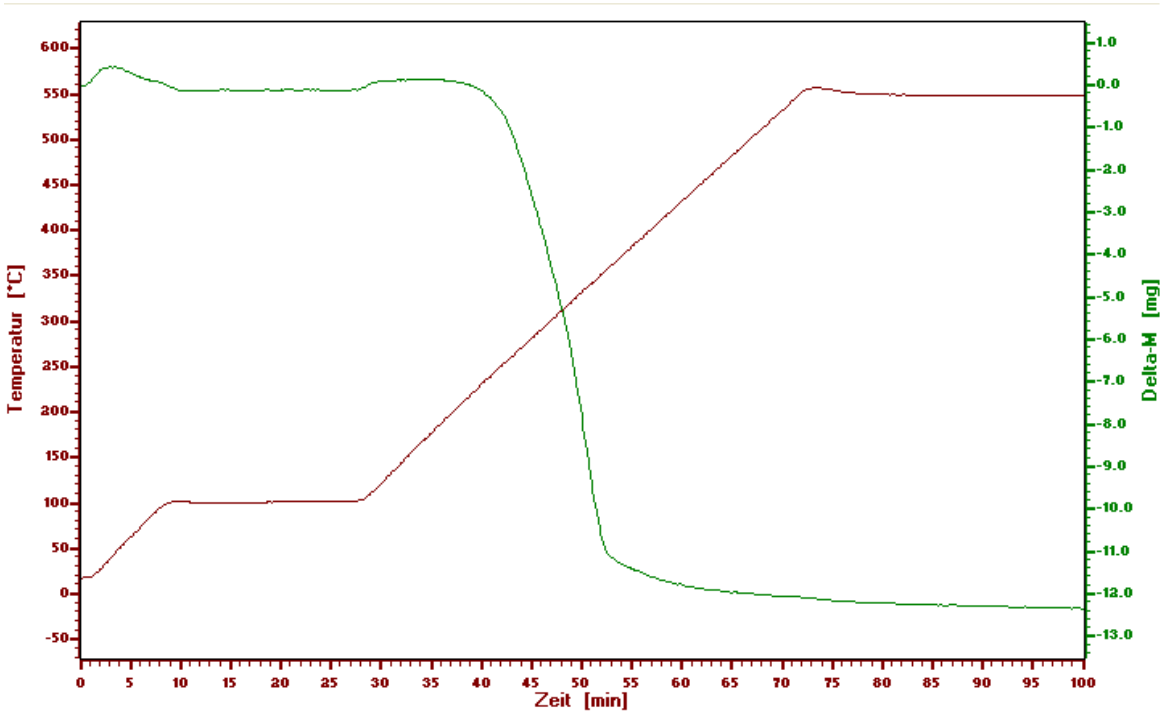

Figure 3.11. Mass loss curve corresponding to heating curve up to 550ºC.

Therefore, three TGA tests with fine powder of beech wood were conducted for different heating rates: 5 K/min, 10 K/min and 15 K/min. All the tests data was displayed in an Excel sheet and, by leading the error between the left and right sides of the Equation (1) to zero, the constants A, E and n were obtained. The results of the TGA tests are shown in the next chapter.

3.3 GC-MS TESTS

Before being injected in the GC-MS machine for chemical compounds evaluation, the local samples taken from the STYX reactor by means of the sampling system must first undergo a preparation.

3.3.1 Injection Preparation

This sample test requires initially ultrasonic agitation during 15 minutes – for suspension and "homogenization" of the water-like and oil-like phases.

After that, the condensate sample was diluted in 8,8 g (10 mL) of Tetrahydrofurane (THF), which is a water-miscible organic solvent that can dissolve a wide range of nonpolar and polar chemical compounds.

Then, depending on the interest of the analysis, the sample should also be doped with the reference species. This procedure enables the comparison of corresponding given surfaces and, hence, the estimation of these species amount inside the sample. In this case, 1 µL of Furfural, 1 µL of Guaiacol

and 10 µL of Phenol should be also added to the sample. The amount of Phenol is considerably high because the GC-MS is less sensitive for recognizing this specie. For qualitative analysis, the injections were simply undoped.

When this final sample is ready, 1 µL of it should be extracted with the GC-MS needle and, then, carefully and precisely injected.

4 RESULTS

This chapter discusses and evaluates the sampling system and sampling method, its technical limitations and proposed modifications. The tests results and pre-results are also presented.

4.1 TGA TESTS RESULTS

The Table 4.1 shows not only the mass losses obtained by the measures with the external precision balance, for the three TGA tests with different heating rates, but also the mass losses detected by the TGA thermal balance.

Table 4.1 – Net initial and final sample masses and mass loss for TGA tests with 5, 10 and 5 K/min.

TGA Test	Heating Rate [K/min]	Net Initial Mass [mg]	Net Final Mass [mg]	Mass Loss [mg]	Remaining Mass [%]	Mass Loss given by TGA Software	Remaining Mass by Software [%]	Error [%]
1	**5**	18,67	3,66	15,01	19,6036	13,55	27,42	3,68
2	**10**	20,5	3,17	17,33	15,4634	14,7	28,29	5,61
3	**15**	20,09	3,94	16,15	19,6117	14,5	27,82	3,90

The plotted TGA curves can be observed in the Figure 4.1 and compared to their data in Table 4.1, according to the corresponding curve color.

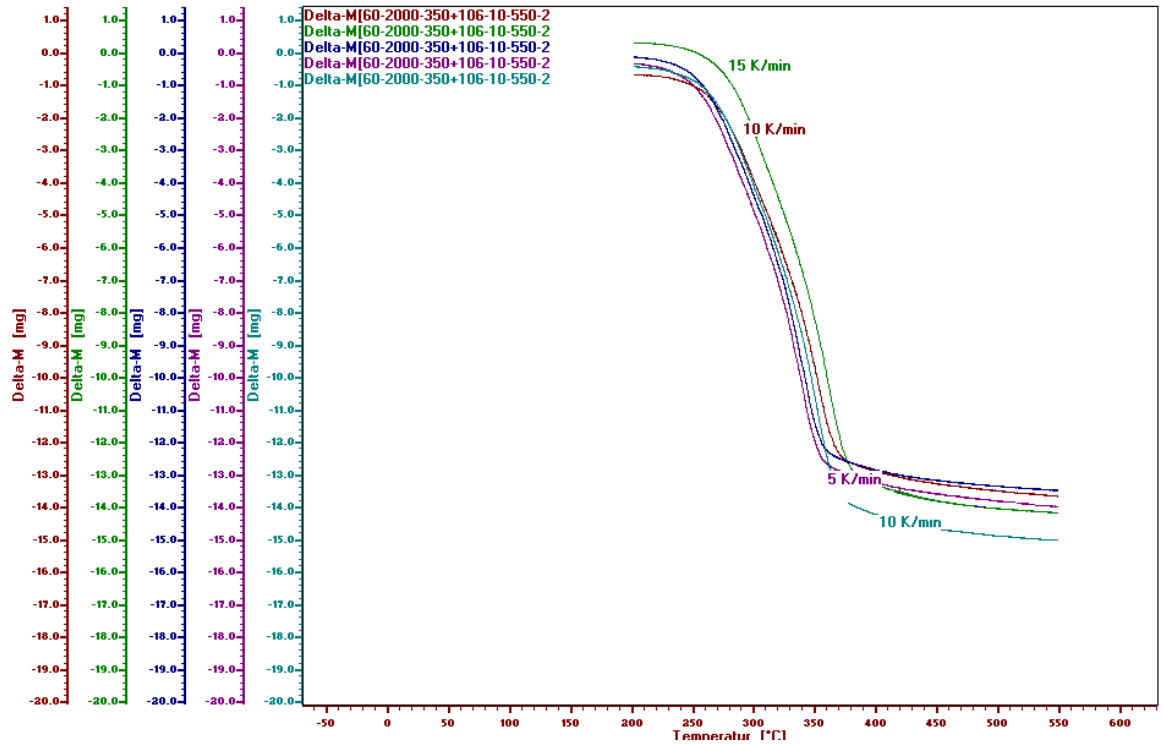

Figure 4.1. Mass loss curves as function of heating program with 5 K/min, 10 K/min and 15 K/min.

Table 4.2 – Normalized Mass Loss Data, α and kinetic reaction calculated based on the TGA test data.

T [°C]	Mass Loss [mg]			Normalized Mass Loss			α			$d\alpha/dt$		
	1	2	3	1'	2'	3'	1	2	3	1	2	3
220	-0,1	0,7	-0,3	0,1	-0,4	-0,1	-0,00738	0,027211	0,006897	-3,1E-05	0,000227	8,62E-05
240	0,1	1,2	0	-0,1	-0,9	-0,4	0,00738	0,061224	0,027586	6,15E-05	0,000283	0,000259
260	0,5	2,4	0,8	-0,5	-2,1	-1,2	0,0369	0,142857	0,082759	0,000123	0,00068	0,00069
280	1,3	4	2,2	-1,3	-3,7	-2,6	0,095941	0,251701	0,17931	0,000246	0,000907	0,001207
300	2,7	6	4,4	-2,7	-5,7	-4,8	0,199262	0,387755	0,331034	0,000431	0,001134	0,001897
320	4,3	8,4	6,4	-4,3	-8,1	-6,8	0,317343	0,55102	0,468966	0,000492	0,001361	0,001724
340	6,4	12	9,6	-6,4	-11,7	-10	0,472325	0,795918	0,689655	0,000646	0,002041	0,002759
360	9	13,7	12,6	-9	-13,4	-13	0,664207	0,911565	0,896552	0,0008	0,000964	0,002586
380	12,3	14,1	13	-12,3	-13,8	-13,4	0,907749	0,938776	0,924138	0,001015	0,000227	0,000345
400	12,8	14,3	13,2	-12,8	-14	-13,6	0,944649	0,952381	0,937931	0,000154	0,000113	0,000172
420	13	14,4	13,3	-13	-14,1	-13,7	0,95941	0,959184	0,944828	6,15E-05	5,67E-05	8,62E-05
440	13,2	14,5	13,4	-13,2	-14,2	-13,8	0,97417	0,965986	0,951724	6,15E-05	5,67E-05	8,62E-05
460	13,3	14,6	13,6	-13,3	-14,3	-14	0,98155	0,972789	0,965517	3,08E-05	5,67E-05	0,000172
480	13,4	14,7	13,7	-13,4	-14,4	-14,1	0,98893	0,979592	0,972414	3,08E-05	5,67E-05	8,62E-05
500	13,45	14,8	13,8	-13,45	-14,5	-14,2	0,99262	0,986395	0,97931	1,54E-05	5,67E-05	8,62E-05
520	13,5	14,9	14	-13,5	-14,6	-14,4	0,99631	0,993197	0,993103	1,54E-05	5,67E-05	0,000172
540	13,55	15	14,1	-13,5	-14,7	-14,5	1	1	1	1,54E-05	5,67E-05	8,62E-05

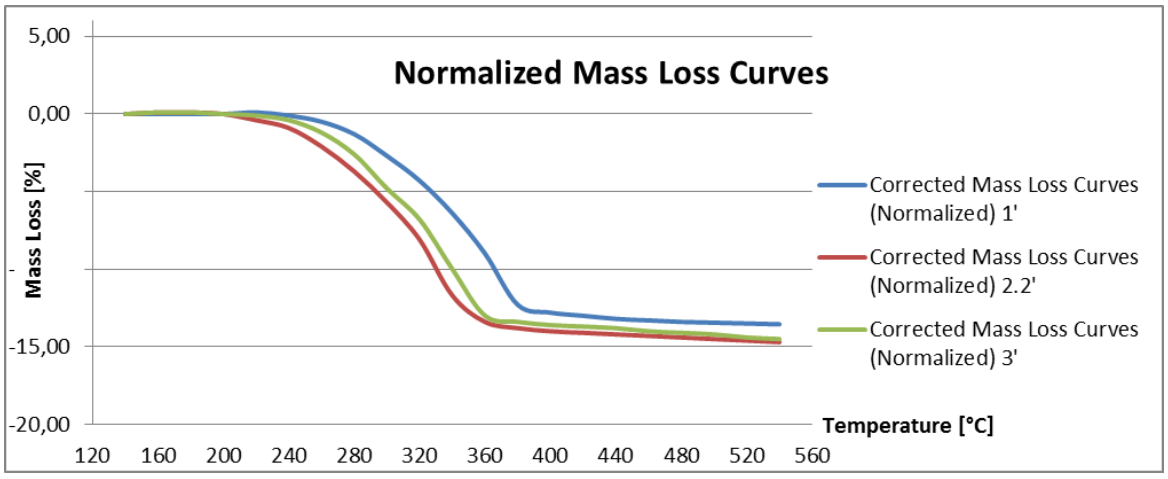

Figure 4.2. Normalized TGA curves

Table 4.3 – Calculation of the right side of Arrhenius Equation for the three different TGA tests and respective errors in relation to the left side values obtained from the curves.

T [°C]	Right Side of Arrhenius Equation			Error		
	Eq. 1	Eq. 2	Eq. 3	1	2	3
	4,66E-06	4,41E-06	4,56E-06	3,76E-09	8,03E-08	6,69E-08
220	2,20E-05	1,96E-05	2,10E-05	1,46E-08	4,62E-07	4,75E-07
240	8,98E-05	7,43E-05	8,15E-05	5,25E-08	8,17E-07	1,45E-06
260	3,12E-04	2,39E-04	2,61E-04	8,80E-08	1,23E-06	3,53E-06
280	9,51E-04	6,26E-04	7,40E-04	-6,63E-07	1,46E-06	2,43E-06
300	2,42E-03	9,36E-04	1,42E-03	-5,44E-06	3,29E-06	5,58E-06
320	4,70E-03	1,24E-03	1,45E-03	-2,15E-05	-6,03E-07	4,59E-06
340	3,68E-03	2,44E-03	3,03E-03	-1,25E-05	-5,92E-06	-9,04E-06
360	5,92E-03	5,09E-03	6,63E-03	-3,50E-05	-2,59E-05	-4,40E-05
380	1,10E-02	1,10E-02	1,49E-02	-1,21E-04	-1,22E-04	-2,23E-04
400	1,68E-02	2,21E-02	3,14E-02	-2,82E-04	-4,88E-04	-9,84E-04
420	2,74E-02	4,05E-02	5,13E-02	-7,53E-04	-1,64E-03	-2,63E-03
440	3,61E-02	6,65E-02	8,99E-02	-1,30E-03	-4,43E-03	-8,09E-03
460	5,06E-02	9,33E-02	1,42E-01	-2,56E-03	-8,71E-03	-2,01E-02
480	5,13E-02	9,46E-02	9,59E-02	-2,63E-03	-8,94E-03	-9,19E-03
500	0,00E+00	0,00E+00	0,00E+00	2,36E-10	3,21E-09	7,43E-09
			Sum:	-7,49E-05	-2,51E-05	-3,49E-05

The minimization of the three total errors sum was performed considering only the highlighted range in Table 4.3 (i.e. for temperatures from 240 to 400°C), where the mass mostly decays. Thus, the obtained kinetic parameters, presented in Table 4.4, also correspond to the tests data from this temperature range.

Table 4.4 – Calculated kinetic constant parameters based on error minimization.

Activation Energy: E =	175 $kJ \cdot mol^{-1}$
Pre-exponential Factor: A =	10E+10
Reaction Order: n =	1

The calculated kinetics parameters were very similar to the parameters given by the correlated literature.

4.2 SAMPLING SYSTEM VALIDATION PRE-RESULTS

4.2.1 Technical limitations and detected operational problems

With the initial filter candles arrangement, it was unfeasible to sample from different reactor positions consecutively, since the shifting from one clean position to another was impossible due to the fact that the clean-side pipeline had to be manually closed.

Thus, the plant had to be switched off and cooled down before performing the next sample at a different point and that turned out to be very impractical and time consuming.

4.2.2 Required Adaptations

In order to solve this operational shifting limitation, an online system of valves with double target was implemented in the filter pipeline (Figure 4.3). This new automation enables not only the consecutive sampling, but also the possibility of re-cleaning the filters during operations. By closing the valve, it is possible to apply the pressure drop required for removing the filter cake which is formed during operations.

Moreover, during the online sampling the short tube is heated up to a temperature above 150°C. Only when this temperature is given by the thermocouple at the inlet of the condenser – meaning that the reactor is operating in steady-state conditions –, the small sampling glass can be switched. Finally, the glass should be removed before switching off the sampling unit.

Figure 4.3. Current arrangement of filter pipeline (with implemented automation)

4.3 RESULTS ANALYSIS

The sample results from the GC-MS analysis have grounded decisions in regard to the definition and validation of the sampling system and method.

The TGA results and calculated kinetic parameters will be useful for the development and validation of a chemical kinetics model for the pyrolysis process in the STYX reactor.

However, in reason of the technical modification in the plant during the last month – to enable the more practical sampling shifting position –, there are still no official sampling campaign results available.

5 CONCLUSION

This chapter presents the final considerations and conclusions about the progress of the sampling system validation.

The main goal of this work – definition and validation of a proper and accurate sampling method for vapors extraction from the STYX Plant – was successfully achieved. The sampling method is applicable to the three positions along the reactor, although the particularities of each position should be considered, and the sampling unit works how expected. The final configuration of the system, as well as the sampling steps, were also well established.

Considering that the STYX Integrated Pyrolysis Plant is a bench-scale plant, it is important to be aware that new challenges usually arise when old problems are solved. In this sense, it is possible to conclude that the plant limitations were identified in time during the sampling method validation and well solved. Currently, the sampling process became more practical and optimized.

Finally, this work enabled the extension of my acquaintances on pyrolysis and provided a great contact with laboratory work and equipment. Therefore, my internship at ITC was a very benefical experience for my studies and also for my professional life.

REFERENCES

[1] Tiberiu M. Leib and Carmo J. Pereira. **Perry's Chemical Engineers' Handbook** (8th Edition), 2008. The Macgrall Hill Companies.

[2] Tomasi Morgano, Marco. **An experimental study for the efficient conversion of biomass into CHP with pyrolysis and hot gas cleaning : mass, energy balances and primary plant analysis**, 2013. ING-IND/09 Sistemi Per L'Energia e L'Ambiente.